OPTIMIZATION OF HOT-PRESSED n-TYPE SiGe/GaP AN I) p-TYPE SiGe/B 'I'1 IERMOELECTRIC MATERIALS

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ABSTRACT

A comprehensive experimental and theoretical work has been conducted in order to optimize the thermoelectric properties of $Si_{80}Ge_{20}$ materials and reach the goal of a combined figure of merit value of 0.85,10-3 K^{-1} averaged over a 600-1000 C temperature range. Improvement for the n-type material has been obtained by determining the optimum amounts of gallium and phosphorus dopants necessary to achieve optimum carrier mobility and concentration. The emphasis is now 011 the consistent reproducibility of these results through understanding and control of the hot-pressing parameters relating microstructure and composition to the transport properties. The optimum doping level has now been firmly established for p-type materials, and work is concentrating on the reduction in thermal conductivity, BN ultra fine particles have been successfully incorporated into fully dense samples and have resulted in desired improvement of the figure of merit. Strongly anisotropic electrical properties have also been discovered and are linked to the hot-pressing process of such ultra-fine particulates.

INTRODUCTION

A substantial effort is underway at both ThermoTrex Corporation (TTC) and the Jet Propulsion Laboratory (JPL) to finalize the optimization of the thermoelectric properties of silicon-germanium (SiGe) alloys used in space power applications at temperatures between 300 and 1000 C [1]. Improvements of n-type materials have focused on determining optimum carrier concentrations, using small additions of gallium ((is) as a way to enhance the solid volubility and the effectiveness of phosphorus (P) dopant in $Si_{80}Ge_{20}$ (SiGe/GaP). It has been demonstrated at both TTC and J]']. that values of the figure of merit, Z, as high as 1 x 10-3 K^{-1} could be achieved in this temperature range. More recent studies have attempted to relate transport properties to

microstructure and composition in a effort to reproducibly obtain such large improvements (2 S-30°/0) over standard P-doped only SiGe (SiGe/P) and baseline 2 mol% GaP doped SiGe (n-MOD/RTG). Development of p-type alloys has concentrated on reducing the thermal conductivity, as optimal doping level [2] can be readily achieved using boron (B). Most of the work was conducted at TTC where a novel technique to prepare ultra fine particulates has been developed [3]. The addition of inert scattering centers into p-type samples (SiGe/B) is expected to result in a Z value of 0.7x1 0-^{3} K-], an improvement of 40% over currently produced material (p-MOD/RTG) and 15-20°/0 over optimally doped samples. Such results on both n- and p-type SiGe would translate in a combined Z value of 0.85x10^{-3} K^{-1}. We will report in this paper on progress made towards these goals

N-TYPE SiGe/GaP A1,1OYS

The systematic preparation at TTC of hot-pressed samples with P:Ga atomic ratios ranging from 6:1 to 1:1 with a total 1) concentration varied between 2 and 3 al .°/O resulted in the determination of optimum conditions for achieving best electrical properties of n-type SiGe/GaP material. Since 1989, 1P], and TTC conducted an extensive characterization of these samples and the changes in electrical resistivity, 1 Hall mobility, carrier concentration and Seebeck coefficient with various high temperature heat treatment conditions. Detailed analysis of microstructure and composition variations under these conditions have also been carried out. Illustrations of these results are presented on figures 1, 2 and 3

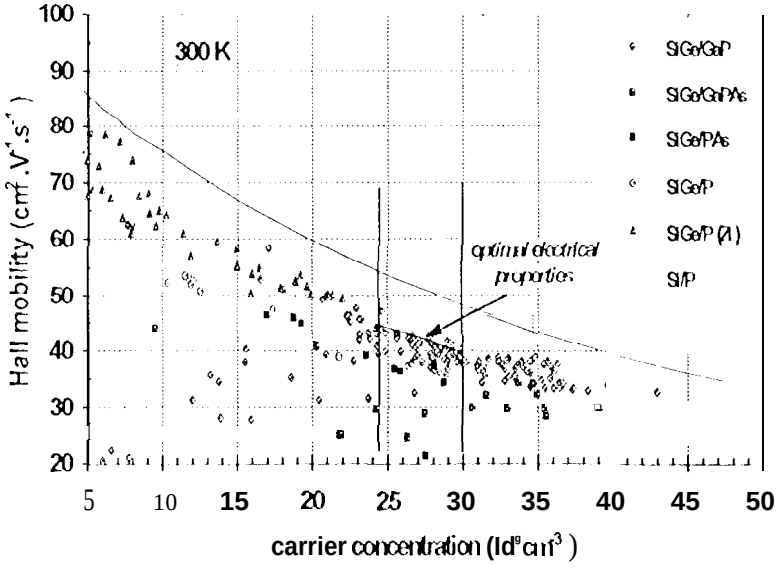


Fig. 1 Room temperature hall mobility of n-type SiGe materials as a function of carrier concentration: optimum electrical properties necessary 10 achieve high figure of remit values are highlighted.

The large carrier concentration increases obtained by heavily doping hot-pressed SiGe samples with several dopants such as Ga, I' and As have been instrumental in the improvement of'the power factor (Seebeck coefficient squared and divided by the electrical resistivity). By doubling the range of room temperature carrier concentrations attained with P-only doping (figure 1), optimization of the electrical properties was made possible. Simultaneous doping with adequate atomic concentrations of Ga and P resulted in up to 300/0 increase in power factor over n-type MOD/RTG materials (figure 2). This is mostly due to a sharp decrease in the electrical resistivity over the 300-1000C temperature range (up to 45%) combined with a smaller decrease in the Seebeck coefficient (up to IS°/O), as seen in figure 3

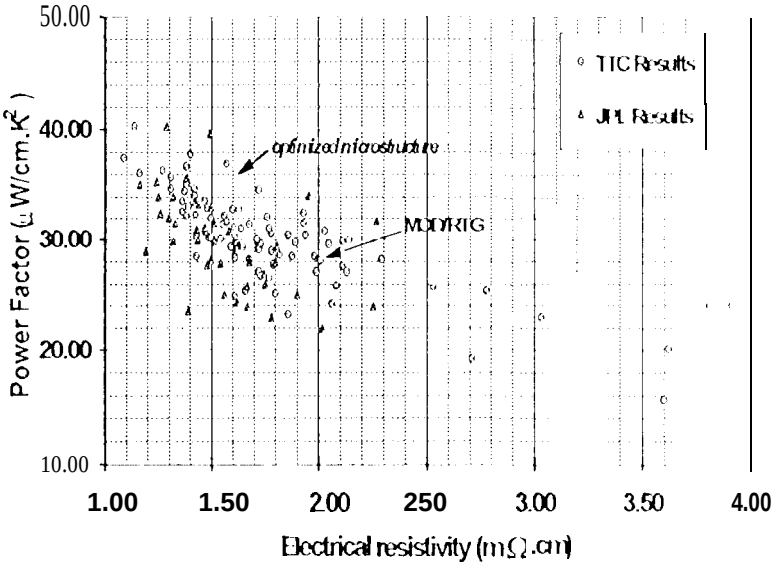


Fig. '2 600-100 0 C integrated average power factor of recent n-type SiGe/GaP samples versus integrated average electrical resistivity.

The experimentally found optimal room temperature electrical properties are highlighted on figure 1 and consist of a) Hall mobility ranging from 45 to 40 $cm^2.V^{-1}.s^{-1}$; b) carrier concentration between 2.5 and $3.0x10^{20}$ cm^{-3}; c) electrical resistivity between 0.55 and $0.52 x10^{-3} \Omega.cm$.

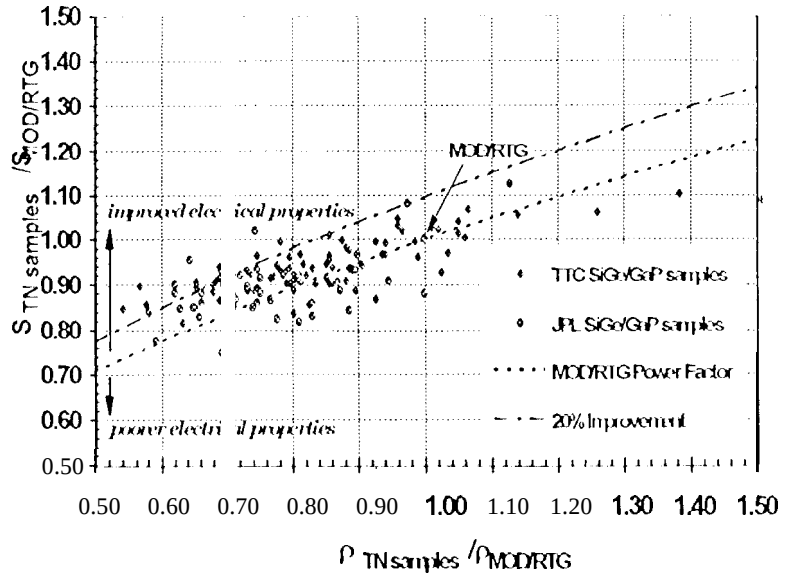


Fig. 3 600-1000 C integrated average properties normalized to MOD/RTG values: power factor of' 1 ecent n-type SiGe/GaP samples versus electrical resistivity.

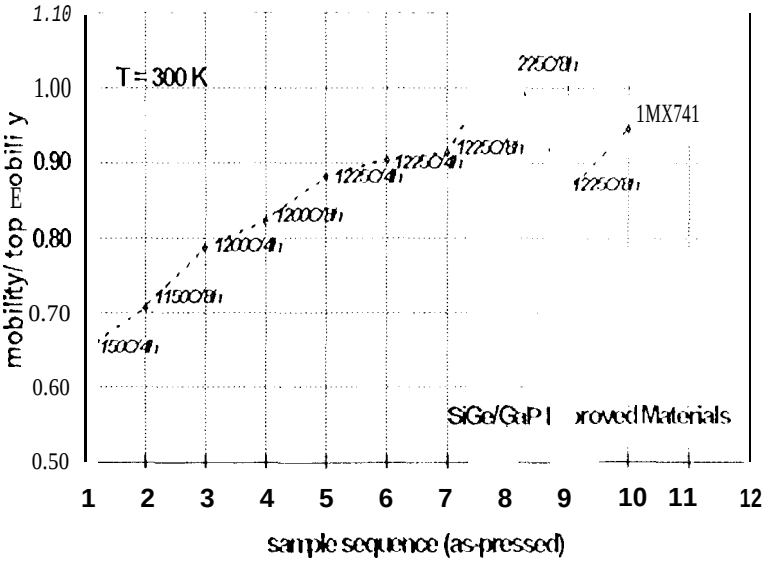
To obtain these properties, the P:Ga ratio must be close to 3:1 with a Ga concentration on the order of 0,75 at.%. The minimal grain size necessary to achieve these high mobility values has been found to be about 20 to 30 µm.

We have reported previously that decrease of mobility with carrier concentration at ion for these heavily doped SiGe/GaP samples was not affected by the additions of Ga, a potential acceptor impurity [1]. We attributed this to the nature of the (is-l' interaction resulting in the creation of Ga-P_n complexes, thus preventing Ga from acting as a compensator and degrading the mobility. Recent results on heavily P-only doped samples prepared by mechanical alloying and subsequent hot-pressing have confirmed this theoretical explanation [4]. The authors reported carrier concentration as high as 3.0×10^{20} cm^{-3}; but no difference in Hall mobility values compared to our SiGe/GaP samples with similar doping levels. This demonstrated that point defect scattering is solely responsible for the lower mobility values obtained in optimized heavily doped SiGe/GaP.

In figures 2 and 3, it is clear that low electrical resistivity values systematically resulted in high power factor values, Also, the magnitude of the reproducible improvement is now about 20%, as larger values can be obtained but are difficult to duplicate with the current processing conditions, Such improvement have been recently confirmed on mechanically alloyed SiGe samples, using similar P and Ga doping concentrations and with 20-50 µm grain

size [5]. Indeed, the successive high temperature heat treatments tend to eventually degrade the electrical properties, but they are still necessary to ensure sufficient grain growth and dopant redistribution in the samples. '1'0 remedy to these difficulties, the current lmt-pressing parameters were changed to obtain substantial grain growth in situ. This can be achieved through longer pressing time and/or higher pressing temperature. However, the loss of dopant in vacuum will increase and must be monitored to remain at desirable levels.

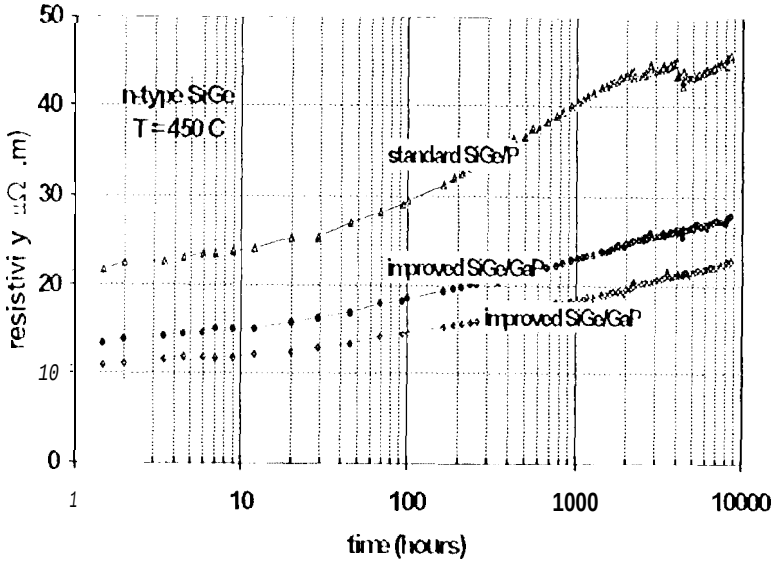
In the standard hot-pressing procedure, samples are pressed at 1150 C for 4 hours. Several new samples wcjc fabricated at temperatures up to 1250 C for times as long as 8 hours. Samples were doped with 3.0 at. °/O 1') and 0.75 at, °/O (is. SEM/EDS results showed that the dopant was retained even under the most aggressive pressing, conditions. The microstructure of the samples pressed at 1200 C and 1225 C is very similar to the one of samples prepared with the standard conditions and heat - treated in air at these very same temperatures. However dopant losses and porosity are much lower for the sample.s prepared by the modified hot-pressing procedures. From room temperature 1 lall effect measurements, the variations of the 1 lall mobility (normalized to the "top mobility" value relative to its carrier concentration) with pressing conditions is plotted on figure 4. It is clear that higher press temperatures and longer times result in improved electrical properties.



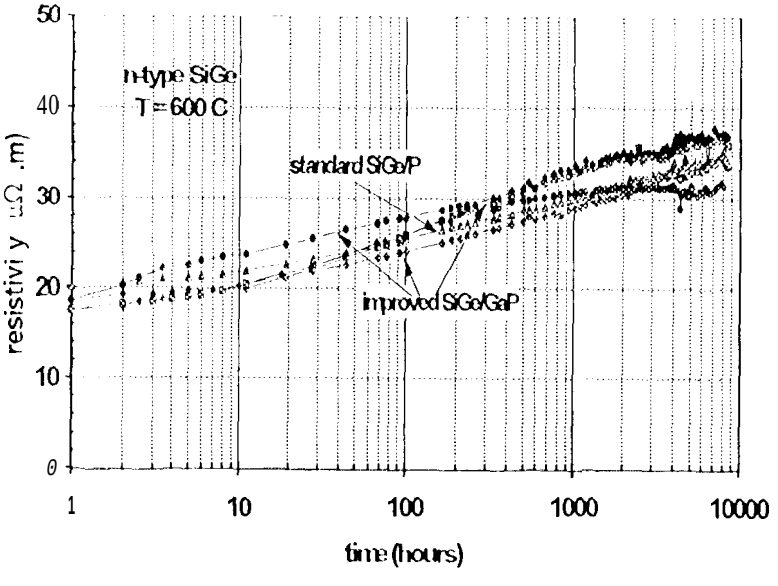
'ig. 4 1 mprovement of room temperature Hall mobility with higher press temperatures and longer press times.

Since the first improved SiGe/GaP samples have been obtained, here has been a persistent worry in the SiGe community that

these high figure of merit values would not hold with time, the improvements disappearing after a short period. Indeed while acknowledging a non-standard behavior, it has been found by several authors that SiGe/GaP MOD/RTG material was inferior to standard P-doped SiGe in the high temperature range [6]. However, such MOD/RTG materials do not present any substantial improvement in Z over standard samples, and the real test should be done with high power factor improved SiGe/GaP samples.

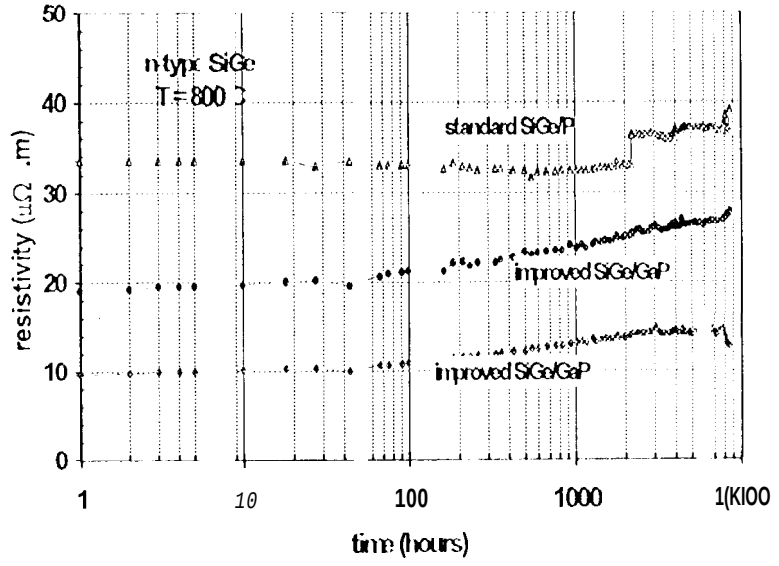


(a)



(b)

We believe that the same mechanisms that resulted in increased 1' solid solubility anti 1' electrical activity will also improve the dopant precipitation data, provided that optimal P:Ga ratio was met. Figures S (a), 5 (b), 5 (c) and 5 (d) display the results of long term resistivit y measurements clone in isothermal furnaces at respective temperature s of 45 0 C, 600 C, 800 C and 1000 C.



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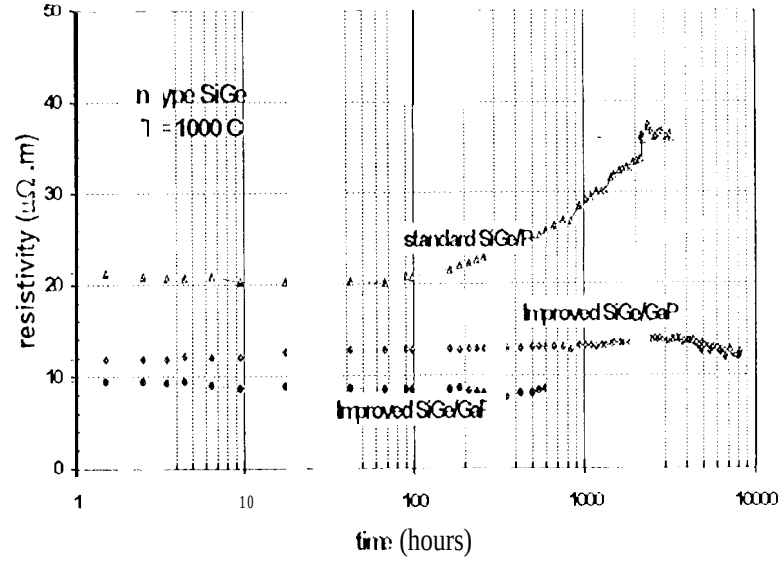

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Fig. 5 Dopant precipitation study of improved n-type SiGe/GaP samples compared to standard P-doped only SiGe samples: data after **8636** hours at temperatures of 450 C (a), 600 C (b), 800 C (c) and 1000((d).

We already reported [7] results on the change of resistivity over time obtained after 1850 hours showing, that the SiGe/GaP samples retained their much lower electrical resistivity (except at 600 C where values are very close together). No significant changes have altered these good results after more than 5600 hours, since at 450 C and 1000 C the rates of resistivity increase are still substantially larger for standard SiGe/P samples, while at 600 C and 800 C these rates are almost identical. These results confirmed that the substantial improvements in power factor over the entire temperature range are retained up to now, especially for the most heavily-dopd samples.

P-TYPE SiGe/B ALLOYS

In order to reduce the thermal conductivity as much as possible, a new phonon scattering mechanism must be added to cover the "gap" in the phonon frequency spectrum left between point defect high frequency phonon scattering and hole-phonon, grain boundary low frequency phonon scattering. Transport properties models have predicted that thermal conductivity values 40% lower could be obtained by adding appropriately sized particles to act as scattering centers for those intermediate frequency phonons that conduct most of the heat through the material [8,9]. These particles should be about 50Å in diameter, and their concentration should be close to 10^{16} cm^{-3}. A larger reduction in the thermal conductivity is expected for the p-type material than for the n-type material since the thermal conductivity reduction in n-type material due to carrier-phonon scattering is larger than the reduction in p-type material. Up until now, it has not been possible to produce such a particulate size and then incorporate it inside the grains of a SiGe alloy. However, a novel spark erosion apparatus has now made this possible. Ultra fine powders of SiGe and that of an inert scattering center can now be produced, mixed and hot-pressed into fully dense samples.

The results obtained for samples fabricated with additions of BN and Si_3N_4 scattering centers respectively are presented on figure 6 and compared with the theoretical predictions. The sample with Si_3N_4 had a thermal conductivity about 30°/0 lower than p-MOD/RTG material, while the sample with the BN particulates only had a 150/0 lower value. However, the sample with Si_3N_4 additions had a much lower carrier concentration because 90% of the B dopant was lost when it reacted with Si_3N_4 The sample with BN centers was more heavily doped than p-MOD/RTG , and comparison with optimally doped SiGe/B samples showed a 15'%0 improvement in the figure of merit, solely due to lower thermal conductivity (same power

factor). Transmission microscope analysis revealed BN centers with diameters of 50-200Å inside $Si_{80}Ge_{20}$ grains typically 2 μm in diameter. The estimated volume fraction of BN **centers** was only 2°/0, lower than the desired 6°/0, but experimental thermal conductivity data was in good agreement with predicted values.

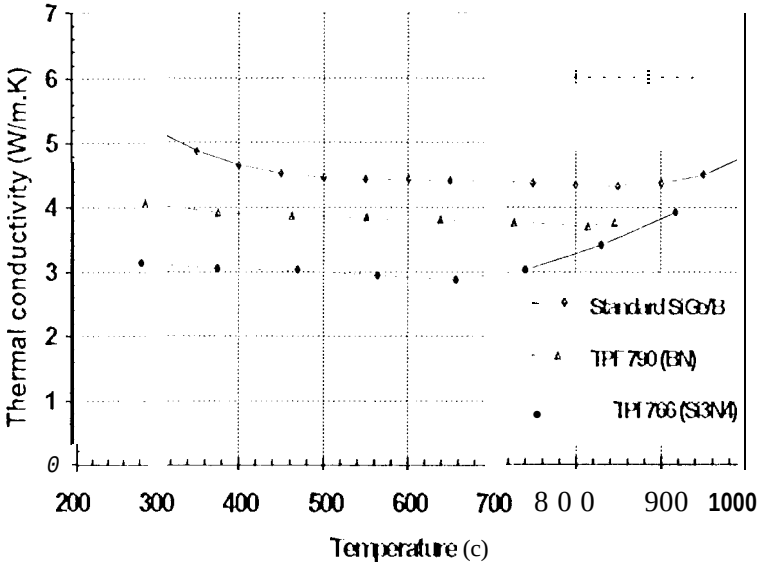

Fig 6 The thermal conductivity of fine particulate p-type SiGe samples with additions of various scattering centers compared to p-MOD/RTG material,

Recent work focused on evaluating more conductive scattering, centers in order to fabricate samples from blended electrodes. By mixing the scattering center and the SiGe in an erosion electrode, the potential for agglomeration of the 50- 100Å scattering inclusions into large clusters has been minimized. B_4C was chosen as a potential candidate based on thermodynamic analysis of its stability relative to B, Si and (it,

While evaluating this sample, significant discrepancies were found in the room temperature electrical resistivity measured on bulk samples (four-point probe method) and thin slices (Van der Pauw method). Because this difference was larger than could be expected from just high temperature quenching effects (dopant precipitation), it appeared as if the sample was geometrically anisotropic. Indeed, measurements of bulk samples (12 mm long and 12.7 mm in diameter) are conducted parallel to the pressing direction while measurements by the Van der Pauw method on thin slices (1 mm thick and 12.7 mm in diameter) are conducted perpendicular to the pressing direction Subsequent examination of the microstructure revealed a highly anisotropic structure with

very long and narrow grains similar to stacked plates observed in the perpendicular directions.

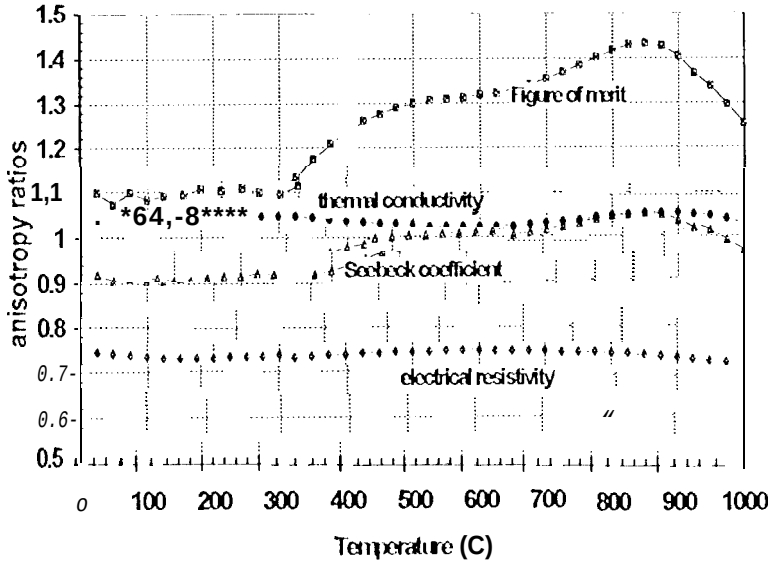

Fig. 7 Perpendicular to parallel anisotropy ratio of the thermoelectric properties of a fine particulate hot-pressed p-type SiGe sample (measurements are usually done parallel to the pressing direction).

This geometrical anisotropy of an otherwise isotropic material (Si-Ge alloys have a cubic structure) leads to a significantly higher mobility and lower electrical resistivity in the perpendicular direction. Because the mobility is the main transport property affected by this effect, the ratio between electrical resistivities in the parallel and perpendicular directions is translated almost directly into the figure of merit. Figure 7 illustrates the resulting relative increase in Z **fbr** this particular sample (maximum Z value increased from $0.4 \times 10\text{-}3\ K^{-1}$ to $0.57.10^{-3}\ K$-]),

Examinations of previous samples show differences also existed, and could be much larger. **in** the past, these differences had been attributed to differences in the quenching procedure for thin slices and bulk samples. Work is ongoing to further quantify the extent of this remarkable anisotropy and to determine the figure of merit of several samples in the perpendicular direction.

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Systematic experimental and theoretical studies on n-type SiGe/GaP materials at both TTC and JPL have resulted in determining the range of microstructure, composition, doping level and electrical properties necessary to achieve improved

power *facto]'* values. 1 :xperiments arc now in progress to optimize the hot-pressing process and obtain these optimal parameters with a minimal amount of heat treatments. Currently reproducible Z values are 0.9 fern-type SiGe/GaP. Optimization of the doping level of p-type SiGe material has resulted in reproducible Z values of 0. S6-0. S9. Addition of ultra fine BN particles to lower the lattice thermal conductivity succeeded in increasing Z up to 0.70.

ACKNOWLEDGMENTS

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